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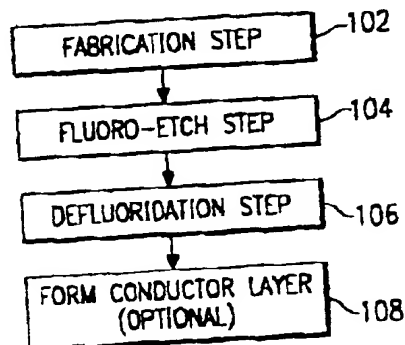
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(54) Improvements in or relating to integrated circuits

(57) An integrated circuit fabrication process in which residual fluorine contamination on metal surfaces

after ashing is removed by exposure to an NH_3/O_2 plasma.

FIG. 1



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Description

FIELD OF THE INVENTION

The present invention relates to integrated circuits and more specifically to fabrication processes comprising post-etch cleanup procedures.

BACKGROUND OF THE INVENTION

During the fabrication of integrated circuits, a wide variety of chemistries are used for etching thin layers. Among the most versatile (and strongest) chemistries are fluorine-based chemistries. Such chemistries are used for oxide etching, for tungsten etching, and (in combination with an oxygen source) for photoresist removal (commonly referred to as "ashing"). However, fluorine-based chemistries tend to leave some fluorine contamination.

The present inventors have discovered that residual fluorine contamination in metal layers is a cause of reduced adhesion, higher contact resistance, and diminished nucleation of subsequently deposited layers. Specifically, the adhesion and electrical contact problems of aluminum which has been exposed to an ashing process are due to formation of metal fluorides and/or oxyfluorides. Furthermore, aluminum in thin films forms a thin but durable native oxide (which is primarily Al_2O_3) on exposure to air, so that the material self-passivates. However, the presence of fluorine contaminants produces a lower density passivation layer, so the self-passivation is not as good. Thus, residual fluorine contamination is a serious problem.

SUMMARY OF THE PRESENT INVENTION

Accordingly a new process is disclosed which substantially removes this fluoride surface contamination, and leaves a more tractable metal oxide layer. This is accomplished by exposure of the fluorine-contaminated surface to NH_3 (or other amine chemistry).

Thus the disclosed inventions provide at least the following advantages: increased adhesion, lower contact resistance, better nucleation of subsequent layers, with resulting greater smoothness and modified surface chemistry; better metal self-passivation; improved corrosion resistance; improved long term chemical stability; and ashing processes can continue to use an admixture of fluorine with the oxygen chemistry.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be further described by way of example, with reference to the accompanying drawings, in which

Figure 1 is a flow chart showing the steps of an exemplary process according to the present invention.

Figures 2A and 2B show a sample metal structure to which the defluorination treatment of Figure 1 can advantageously be applied.

Figure 3 shows a sample via structure to which the defluorination treatment of Figure 1 can advantageously be applied.

Figures 4A-4C show a sample micromechanical structure to which the defluorination treatment of Figure 1 can advantageously be applied.

Figure 5 shows a sample metal structure utilizing an ashing step to which the defluorination treatment of Figure 1 can advantageously be applied, and

Figures 6A-6D are characterization results which demonstrate how the process of Figure 1 operates.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The numerous innovative teachings of the present invention will be described, by way of example, with particular reference to a preferred embodiment thereof. However, it should be understood that this embodiment provides only a few examples of the many advantageous uses of the innovative teachings disclosed herein.

In order to eliminate the adhesion problems associated with the presence of fluorine contaminants, a process for the low temperature removal of fluorides and oxyfluorides produced from fluorine-laden plasma processes, such as that produced by a long undercut process in a micromechanical process, from metal-oxide surfaces is preferably used. Removal of fluorine from, for example, electrode surfaces permits the formation of a higher density passivation layer, since more bonding sites for passivants become available due to the absence of the fluorine. Metal fluorides and oxyfluorides are known to be more volatile compared to their oxides and are more prone to corrosion attack. Aluminum fluoride is also a stronger Lewis acid (and hence less inert) than aluminum oxide. The removal of fluorine improves the long term chemical stability of such surfaces and reduces their reactivity.

Figure 1 shows a flow chart illustrating the steps in an exemplary process embodiment, and Figures 2A and 2B show a sample metal structure to which such defluorination treatments can advantageously be applied.

In Figure 1, step 102 shows fabrication steps before the fluoro-etch. In the sample implementation of Figure 2A, this includes the formation of an underlying metal layer 200, typically aluminum, formation of a dielectric layer 210 (e.g. SiO_2), and formation and patterning of a photoresist layer 220.

Step 104 shows the fluoro-etch step. In the sample implementation of Figure 2A, this would include etching of the SiO_2 210 through the mask of photoresist layer 220, followed by removal of the photoresist layer 220, by a remotely excited NF_3/O_2 plasma in a Gasometrics TM asher.

Step 106 shows the defluorination step performed by one of the various embodiments detailed below.

Step 108 shows the optional subsequent step of forming an overlying barrier/adhesion layer 225 and conductor layer 230 as can be seen in Figure 2B. Due to the defluorination performed by step 106, this subsequent step will achieve better adhesion, lower contact resistance and/or better nucleation (and hence smoothness) of subsequently deposited layers.

For example a sample embodiment demonstrates the use of an NH_3 plasma generated in a RIE plasma reactor at room temperature to remove the fluorides and oxyfluorides from AlO_xF_y surfaces. These fluorine-laden surfaces are generated by an NF_3/O_2 ashing process.

The following tables give results from actual fluorine removal test runs utilizing sample embodiments of the processes described herein. The table below shows a preferred embodiment of a method where an NH_3/O_2 plasma is used. (The use of an oxidizing component helps to convert the oxyfluorides to oxides.) Flow was not directly regulated, but a mechanical pump was used to roughly regulate the total pressure. (This procedure was performed in a Technics MicroRIE-800 etcher.)

Starting Material	AlO_xF_y
Gas ratio	NH_3/O_2 1:1
Total pressure	600 mTorr
RF power	70 W
Time	10 min

Surface fluorine concentration was markedly reduced, and surface oxygen concentration was increased, as shown by the fourth (bottom) trace in Figure 6A.

The following tables demonstrate less preferred embodiments utilizing only an NH_3 plasma.

Starting Material	AlO_xF_y
Total pressure	300 mTorr
RF power	70 W
Time	15 min

Again, surface fluorine concentration was markedly reduced, as shown by the third trace in Figure 6A.

Note that in the table shown below, the surface was exposed to an NH_3 plasma for only one-third of the time used in the preceding run. Nevertheless, the fluorine concentration was greatly reduced, as shown in the second curve of Figure 6A.

Starting Material	AlO_xF_y
Total pressure	300 mTorr

(continued)

RF power	70 W
Time	5 min

Sample Embodiment: Al Defluorination with Aqueous NH_4OH

In another sample embodiment, defluorination of the surface was accomplished using an aqueous NH_4OH solution (or vapor). As detailed in the experimental results below, this process has been found to achieve successful defluorination of the aluminum surface.

Alternative Embodiment: Al Defluorination with Non-Aqueous Liquid Reagent

In another sample embodiment, defluorination of the surface was accomplished using a non-aqueous liquid (1%wt of tetramethylammonium hydroxide in ultrapure methanol). This process too has been found to achieve successful defluorination of the aluminum surface.

Alternative Embodiment: Atomic Hydrogen

In this contemplated alternative embodiment, a mixture of atomic hydrogen and activated H_2 (as afterglow from a microwave excitation stage) is used, instead of an amine chemistry, as the fluorine scavenger.

Alternative Embodiment: N_2O

In this sample alternative embodiment, N_2O is used rather than O_2 in combination with NH_3 or another fluorine scavenger, as an oxidizing component. Other processing conditions remain substantially the same.

Alternative Embodiment: H_2O

In this sample alternative embodiment, H_2O is used rather than O_2 in combination with NH_3 or another fluorine scavenger, as an oxidizing component. Other processing conditions remain substantially the same.

Alternative Embodiment: Ozone

In this sample alternative embodiment, O_3 is used rather than O_2 in combination with NH_3 or another fluorine scavenger, as an oxidizing component. Other processing conditions remain substantially the same.

Alternative Embodiment: Via Treatment

For example, the innovative processes disclosed herein are applicable to defluorination of conductor sur-

faces after a tungsten etchback step. (Tungsten etchback normally uses a fluorine-based chemistry.) Figure 3 shows a sample implementation of a via structure using the innovative treatment process.

In this embodiment, an interlevel dielectric layer 310 (typically SiO_2) is deposited over an underlying metal layer 300 (typically aluminum). Thereafter, the dielectric layer is patterned using a photoresist layer and etched using a fluoro-etch to form holes where vias are desired (i.e. where an electrical contact to the underlying metal layer 300 is desired). This etching step leaves residual fluorine on the surface of the underlying metal, which can then be removed using one of the defluorination processes described above. A diffusion barrier layer 320, such as titanium nitride, can then optionally be deposited to line the walls of the vias before depositing metal 330 (tungsten in this example) overall. Global etchback then leaves the tungsten as plugs. Additional metal layers 340 can be deposited and etched.

Alternative Embodiment: Undercutting

Figures 4A-4C show another sample structure to which the disclosed defluorination treatments can advantageously be applied. In this alternative embodiment, an optical modulator cell 400 includes a plate of aluminum 410 which is suspended over a well 420 of a dielectric material, such as SiO_2 , as shown in the plan view of Figure 4A.

At an intermediate stage of fabrication, this plate 410 overlies a layer of photoresist 430, which has been deposited over well bottom 420. Figure 4B illustrates this configuration. An interlevel dielectric layer 450 is shown adjacent to the photoresist layer, and a layer of mirror material 460 rests on top of the plate 410. The photoresist layer 430 is subsequently removed, by an isotropic oxyfluorine undercut process (similar to an ashing process), leaving the micromechanical structure shown in Figure 4C. This step also leaves residual fluorine on the surface of the metal 410 and 440. This can cause problems, as discussed above. In order to obviate these problems, the residual fluorine is then removed using one of the innovative defluorination processes described above.

Alternative Embodiment: Ashing

Integrated circuit fabrication processes use many photoresist patterning steps at various stages, and photoresist patterning steps are normally followed by an "ashing" step to remove the photoresist. The ashing step uses an oxygen plasma to volatilize the organic components of the photoresist, but also normally include some admixture of fluorine to volatilize the unavoidable fraction of inorganics (the "ash").

Thus, any ashing step tends to introduce superficial fluorination (at least on surfaces which form a nonvolatile fluoride or oxyfluoride). For example, in Figure 5, a

metal structure is shown consisting of a transistor 500 contacted by a metal layer 510, such as aluminum. An interlevel dielectric layer 530 overlies the transistor. Preferably, the layer 530 comprises BPSG/TEOS. Also shown is a LOCOS oxide 540. The metal layer can be patterned and etched using a photoresist 550 followed by an ashing step to remove the photoresist 550. The ashing step will leave some residual fluorine 560 on the surface of the metal layer 510. Therefore, the disclosed defluorination chemistries can also be used in this context to remove the residual fluorine to provide improved adhesion for subsequently deposited layers.

Figures 6A-6D show X-ray Photoelectron Spectroscopy (XPS) measurements which demonstrate how the surface fluorine concentration is affected by the steps described above.

The effectiveness of an NH_3 plasma treatment is shown in Figure 6A. Again, evidence for the removal of fluorine (present as aluminum oxyfluoride and aluminum fluoride) and the increase in oxygen (present as aluminum oxide) is clearly evident. Some contamination (mainly Na) is observed and is attributed to contamination of the reactor walls. The use of an NH_3/O_2 plasma was shown to be very effective at fluorine removal and oxide formation, as is also seen in Figure 6A.

The top trace in Figure 6A shows the high levels of fluorine on the surface of the aluminum after five passes through the Gasonics asher. The second, third, and fourth traces show the effect of the plasma defluorination processes described above; note how the height of the fluorine peaks is reduced, and that of the oxygen peaks is increased.

Residual fluorine present in the reactor can result in a lower limit in the removal of fluorine from the surface. This effect is shown in Figure 6B, where it can be seen that the fluorine lines after defluorination are still higher than those in as-received aluminum. As shown by the small peak marked Na, some sodium contamination was also observed.

The importance of ions in the process was examined by using a screen placed over a fluorinated sample. (Under these conditions the screen served as an "ion shield".) Without such a shield, fluorine removal is observed, as indicated in the second trace of Figure 6C for the NH_3/O_2 process. When the shield is in place, little or no removal occurs, as shown in the third trace of Figure 6C. These results suggest that ions present in the plasma are important for effective defluorination of the surface.

Figure 6D shows two further points. As the bottom two traces show, the surface fluorine contamination appears to saturate after just one pass through an NF_3/O_2 remote plasma generated in a Gasonics etcher, with no significant increase seen after four further passes through this process.

Figure 6D also shows the effectiveness of defluorination in aqueous NH_4OH solution. Exposing a fluorine-contaminated surface to an aqueous NH_4OH solution

for 1 min results in the removal of fluorine from the surface and a concomitant increase in aluminum oxide formation. The surface produced by this process also appears to reflect light in a specular manner, indicating that the surface roughness can be controlled. Note that exposure to NH_4OH vapor for one hour achieved some fluorine reduction, but was far less effective.

The exemplary embodiments provide: A defluoridation process, comprising the steps of: (a) providing a layer of conductive material having fluorides and/or oxyfluorides on the surface thereof; and (b) after said step (a) removing said fluorides and said oxyfluorides from the surface of said layer of conductive material, using a fluorine-scavenging chemistry, whereby improved adhesion for subsequently deposited layers is achieved.

There is also provided: A defluoridation process for fabricating integrated circuit structures, comprising the steps of: (a) forming a layer of conductive material; (b) performing an etching step which leaves residual fluorine on the surface of said layer of conductive material; and (c) after said step (b), removing said residual fluorine with an amine chemistry, whereby improved adhesion for subsequently deposited layers is achieved.

There is yet further provided: An integrated circuit fabrication process, comprising the steps of: (a) forming underlying structures; (b) forming at least one interlevel dielectric layer over said underlying structures; (c) patterning and etching said dielectric layer to form holes in contact locations, wherein said step of etching leaves residual fluorine on the surface of said dielectric layer and said underlying structures; and (d) after said step (c), removing said residual fluorine by reacting with a plasma-activated fluorine-scavenging chemistry, whereby improved adhesion for subsequently deposited layers is achieved.

As will be recognized by those skilled in the art, the innovative concepts described herein can be modified and varied over a tremendous range of applications, and accordingly the scope of the subject matter should not be limited by any of the specific exemplary teachings given.

The defluoridation reagent is preferably in the vapor phase, but can alternatively be in the liquid or supercritical phase.

Alternatively, the disclosed chemistries can also be applied to other metals which have been exposed to a fluorine-bearing gas flow, if the metal oxide is more tractable than a metal oxyfluoride.

Of course, the specific etch chemistries, layer compositions, and layer thicknesses given are merely illustrative, and do not by any means delimit the scope of the claimed invention.

Some additional background, which shows the knowledge of those skilled in the art, regarding process modifications and implementations, may be found in the following books: Anner, *PLANAR PROCESSING PRIMER* (1990); BICMOS TECHNOLOGY AND APPLICATIONS (ed. Alvarez 1989); Brodie and Muray, *PHYSICS OF MICROFABRICATION* (1982); Castellano, *SEMI-*

CONDUCTOR DEVICE PROCESSING TECHNOLOGY TRENDS IN THE VLSI ERA (1991); Chen, *CMOS DEVICES AND TECHNOLOGY FOR VLSI*; Cooper and Weisbecker, *SOLID STATE DEVICES AND INTEGRATED CIRCUITS* (1982); Dillinger, *VLSI ENGINEERING* (1988); DRY ETCHING FOR VLSI (ed. van Roosmalen et al. 1991); Einspruch et al., *LITHOGRAPHY FOR VLSI* (1987); El-Kareh et al., *INTRODUCTION TO VLSI SILICON DEVICES* (1986); Elliott, *INTEGRATED CIRCUIT MASK TECHNOLOGY* (1985); Elliott, *INTEGRATED CIRCUIT FABRICATION TECHNOLOGY* (ca. 1983, and 2 ed. 1989); *ENCYCLOPEDIA OF SEMICONDUCTOR TECHNOLOGY* (ed. Grayson 1984); Ferry et al., *ULTRA LARGE SCALE INTEGRATED MICROELECTRONICS* (1988); Gise and Blanchard, *MODERN SEMICONDUCTOR FABRICATION TECHNOLOGY* (1986); *HANDBOOK OF SEMICONDUCTOR TECHNOLOGY* (ed. O'Mara et al. 1990); *HANDBOOK OF THIN FILM PROCESS TECHNOLOGY* (Institute of Physics, annual editions); *HANDBOOK OF VLSI MICROLITHOGRAPHY, PRINCIPLES, TECHNOLOGY, AND APPLICATIONS* (ed. Glendinning and Helbert 1991); Knights, *PHYSICS OF VLSI* (1984); Kooi, *INVENTION OF LOCOS* (1991); LPCVD SILICON NITRIDE AND OXYNITRIDE FILMS (ed. Habraken); Maly, *ATLAS OF INTEGRATED CIRCUIT TECHNOLOGIES* (ca. 1985); *MICROELECTRONICS PROCESSING* (ed. Jensen); Milnes, *SEMICONDUCTOR DEVICES AND INTEGRATED ELECTRONICS* (1980); Muller & Kamins, *DEVICE ELECTRONICS FOR INTEGRATED CIRCUITS* (1977, 2 ed. 1986); Nashelsky and Boylestad, *DEVICES, DISCRETE AND INTEGRATED* (1981); Nicollian and Brews, *MOS PHYSICS AND TECHNOLOGY* (ca. 1983); *PHYSICS AND FABRICATION OF MICROSTRUCTURES AND MICRODEVICES* (ed. Kelly et al. 1986); Pierret, *FIELD EFFECT DEVICES* (1983 and 2 ed. 1990); Pimbley et al., *ADVANCED CMOS PROCESS TECHNOLOGY* (1989); *PLASMA ETCHING* (ed. Manos and Flamm 1989); *PLASMA PROCESSING* (ed. Dieleman et al. 1992); *POWER INTEGRATED CIRCUITS, PHYSICS, DESIGN, AND APPLICATIONS* (ed. Antognetti 1986); Prince, *SEMICONDUCTOR MEMORIES: DESIGN, MANUFACTURE* (2 ed. 1991); *QUICK REFERENCE MANUAL FOR SI INTEGRATED CIRCUIT TECH* (Beadle, Tsai, and Plummer); *SEMICONDUCTOR TECHNOLOGY HANDBOOK* (ed. Trapp et al., 1st through 6th editions); Rao, *MULTILEVEL INTERCONNECT TECHNOLOGY* (ca. 1993); Runyan and Bean, *SEMICONDUCTOR INTEGRATED CIRCUIT PROCESSING TECHNOLOGY* (1990); Sedra and Smith, *MICROELECTRONIC CIRCUITS* (3rd ed. 1991); Schmitz, *CVD OF TUNGSTEN AND TUNGSTEN SILICIDES FOR VLSI/ULSI APPLICATIONS* (1992); *SEMICONDUCTOR PROCESSING* (ed. Gupta 1984); Stern, *FUNDAMENTALS OF INTEGRATED CIRCUITS*; Streetman, *SOLID STATE ELECTRONIC DEVICES* (2 ed. 1980 and 3 ed. 1990); Sze, *PHYSICS OF SEMICONDUCTOR DEVICES* (1969, and 2 ed.

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Claims

1. A deflouridation process, comprising the steps of:

providing a layer of conductive material having flourides and/or oxyflourides on a surface thereof; and

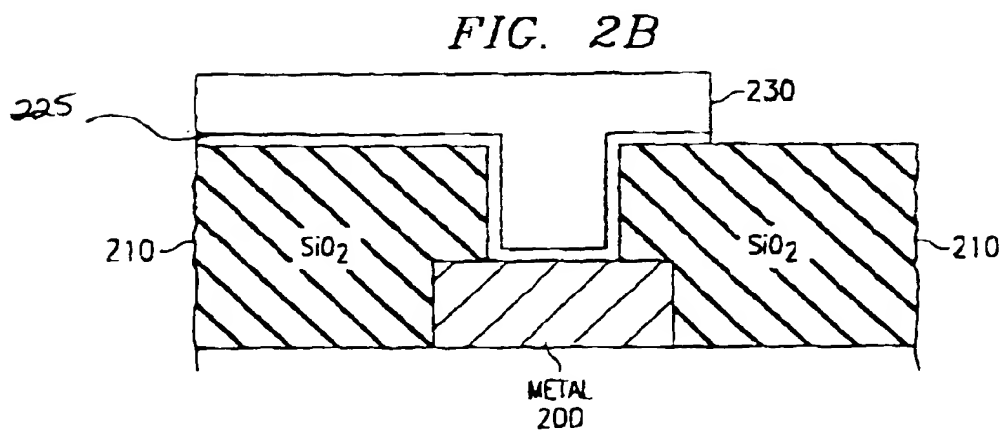
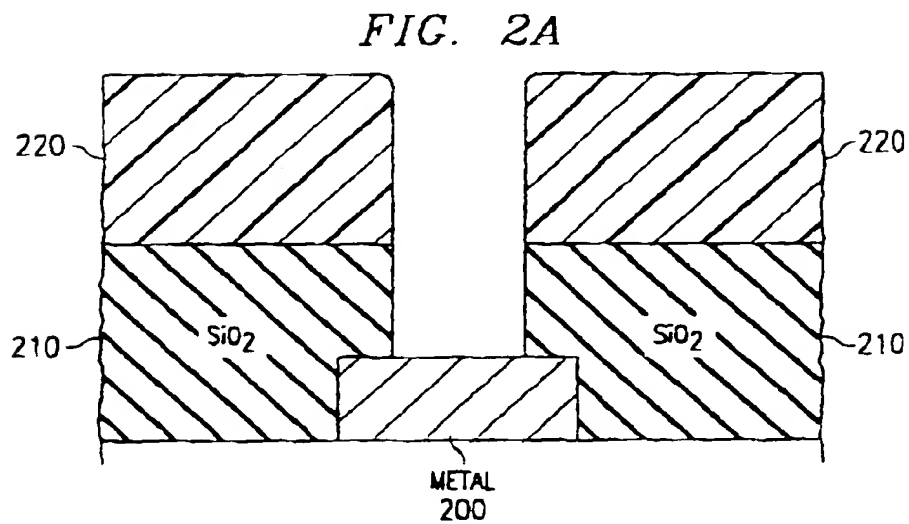
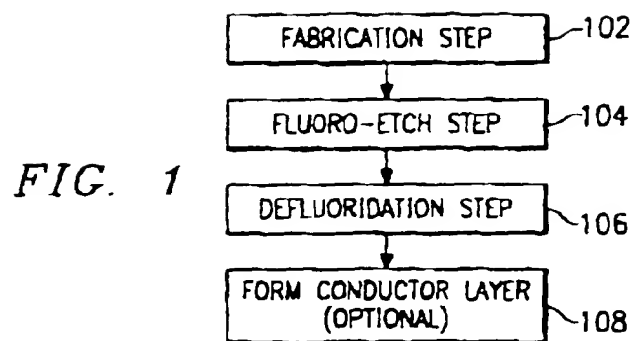
removing said flourides and said oxyflourides from the surface of said layer of conductive material, using a flourine-scavenging chemistry to thereby improve adhesion for subsequently deposited layers is achieved.

2. The process of Claim 1, further comprising the step of, after said step of removing, depositing an overlying conductor layer.
3. The process of Claim 1 or Claim 2, wherein said step of removing comprises using an NH_3 plasma.
4. The process of Claim 1 or claim 2, wherein said step of removing comprises using NH_4OH wet chemistry.
5. The process of Claim 1, wherein said step of providing said layer of conductive material comprises providing aluminum.
6. A deflouridation process for fabricating integrated circuit structures, comprising the steps of

forming a layer of conductive material;
performing an etching step which leaves residual flourine on a surface of said layer of conductive material; and

removing said residual flourine with an amine chemistry to thereby improve adhesion for subsequently deposited layers.

7. The process of Claim 6, further comprising the step, after said step of removing, depositing an overlying conductor layer.
8. The process of Claim 6 or Claim 7, wherein said step of removing comprises using a plasma-activated chemistry.
9. The process of Claim 6 or Claim 7, wherein said step of removing comprises using NH_4OH wet chemistry.
10. The process of Claim 6 or Claim 7, wherein said step of removing comprises using as non-aqueous amine wet chemistry.
11. The process of any of Claims 6 to 10, further comprising: performing said step of removing at room temperature.
12. The process of any of Claims 6 to 11, wherein said etching step comprises using an oxyflourine ashing technique for removing said photoresist.
13. An integrated circuit fabrication process, comprising the steps of:
- forming at least one interlevel dielectric layer over an underlying structure;
patterning and etching said dielectric layer to form holes in contact locations, wherein said step of etching leaves residual flourine on the surface of said dielectric layer and said underlying structures; and
removing said residual flourine by reacting with a plasma-activated flourine-scavenging chemistry to thereby improve adhesion for subsequently deposited layers.
14. The process of Claim 13, further comprising the step, after said step of removing, of depositing an overlying conductor layer.
15. The process of Claim 13 or Claim 14, wherein said step of removing comprises using an NH_3 plasma.



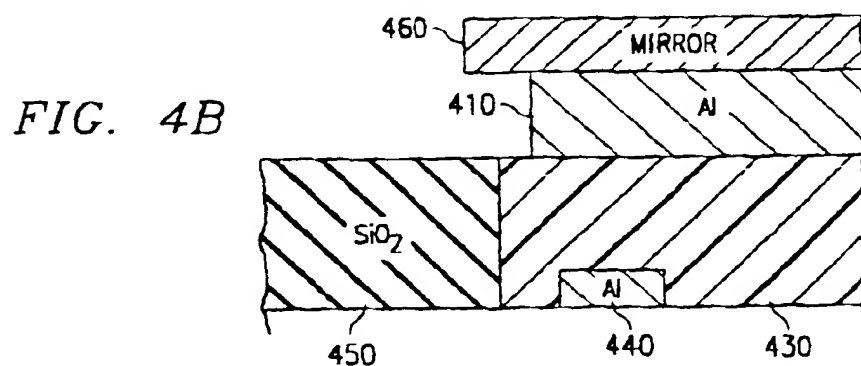
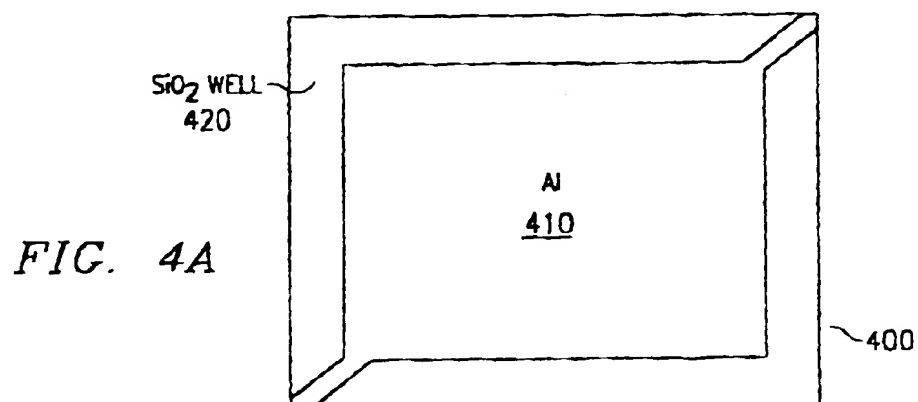
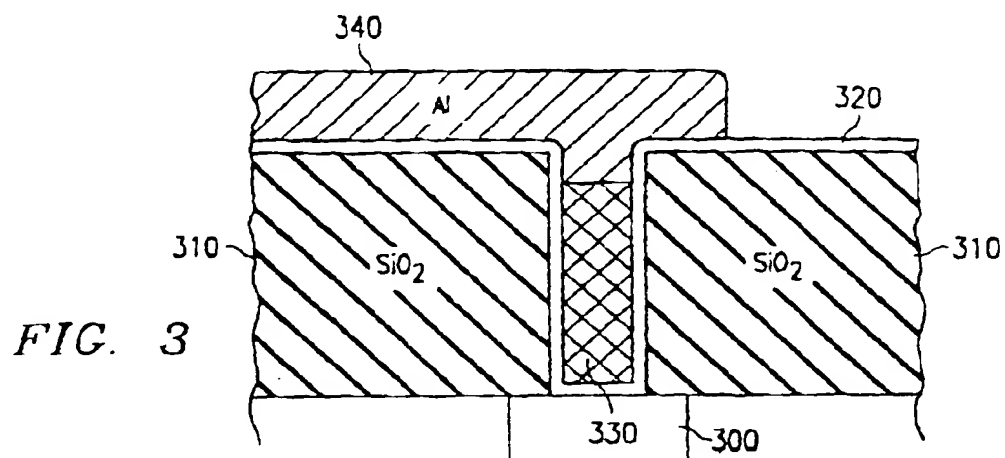


FIG. 4C

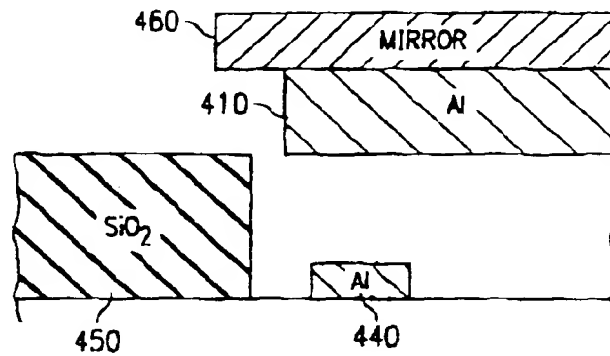
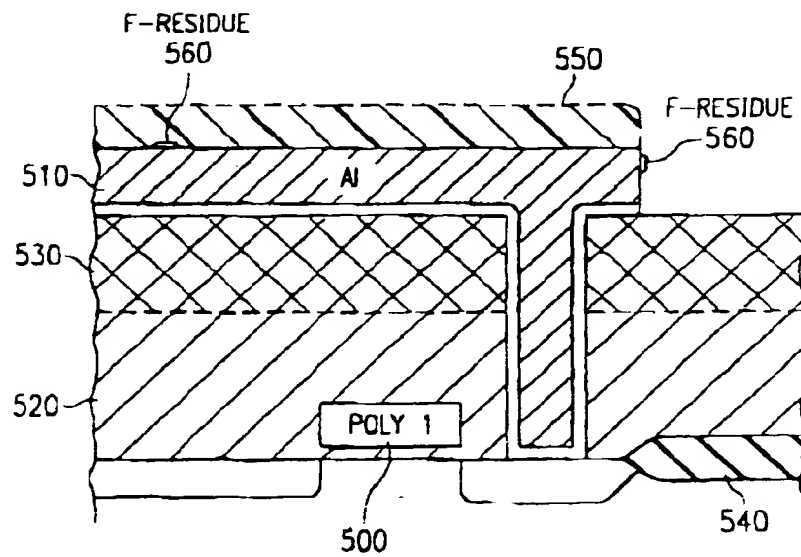


FIG. 5



PLASMA REMOVAL OF F FROM DMD ASHED ALUMINUM

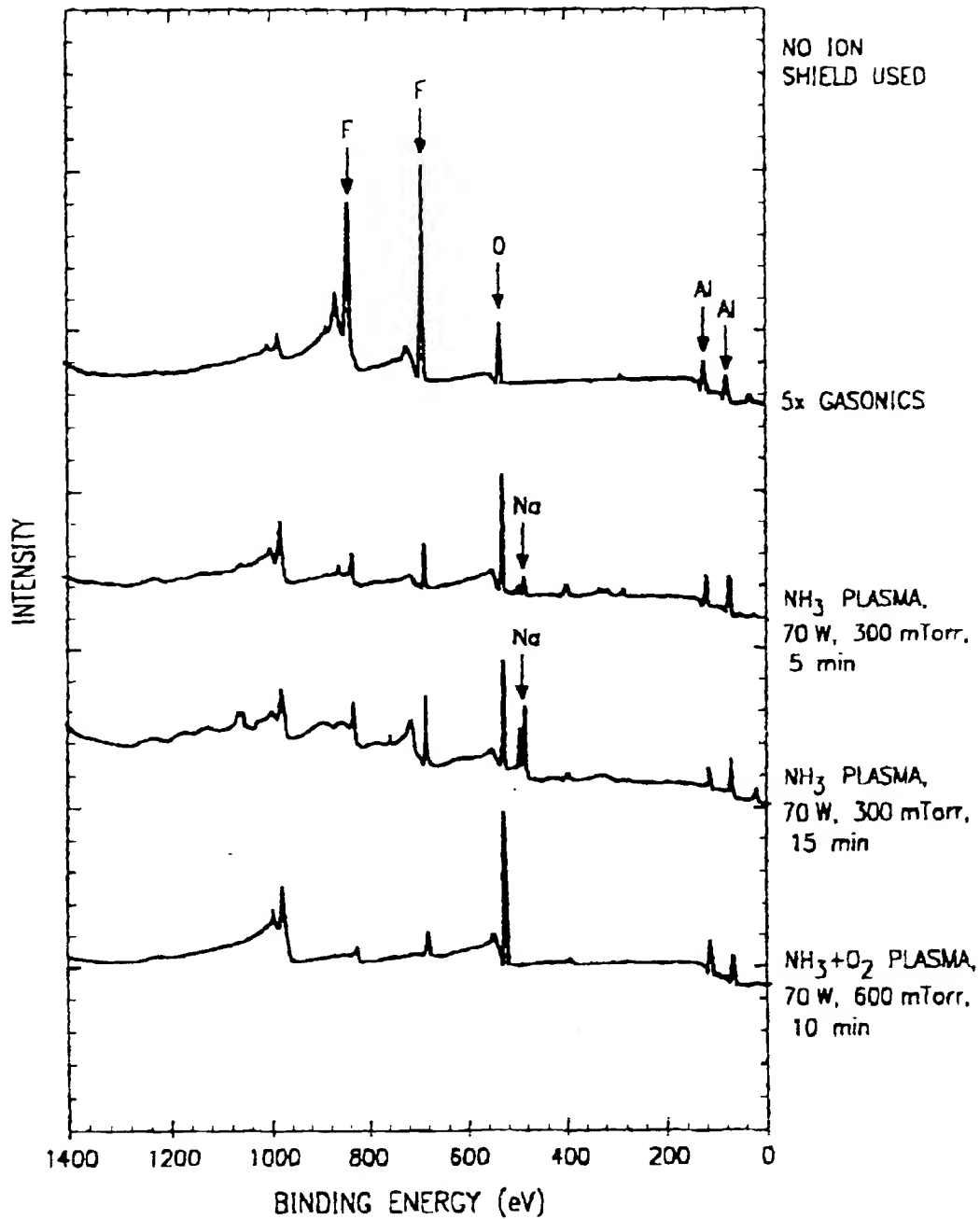


FIG. 6A

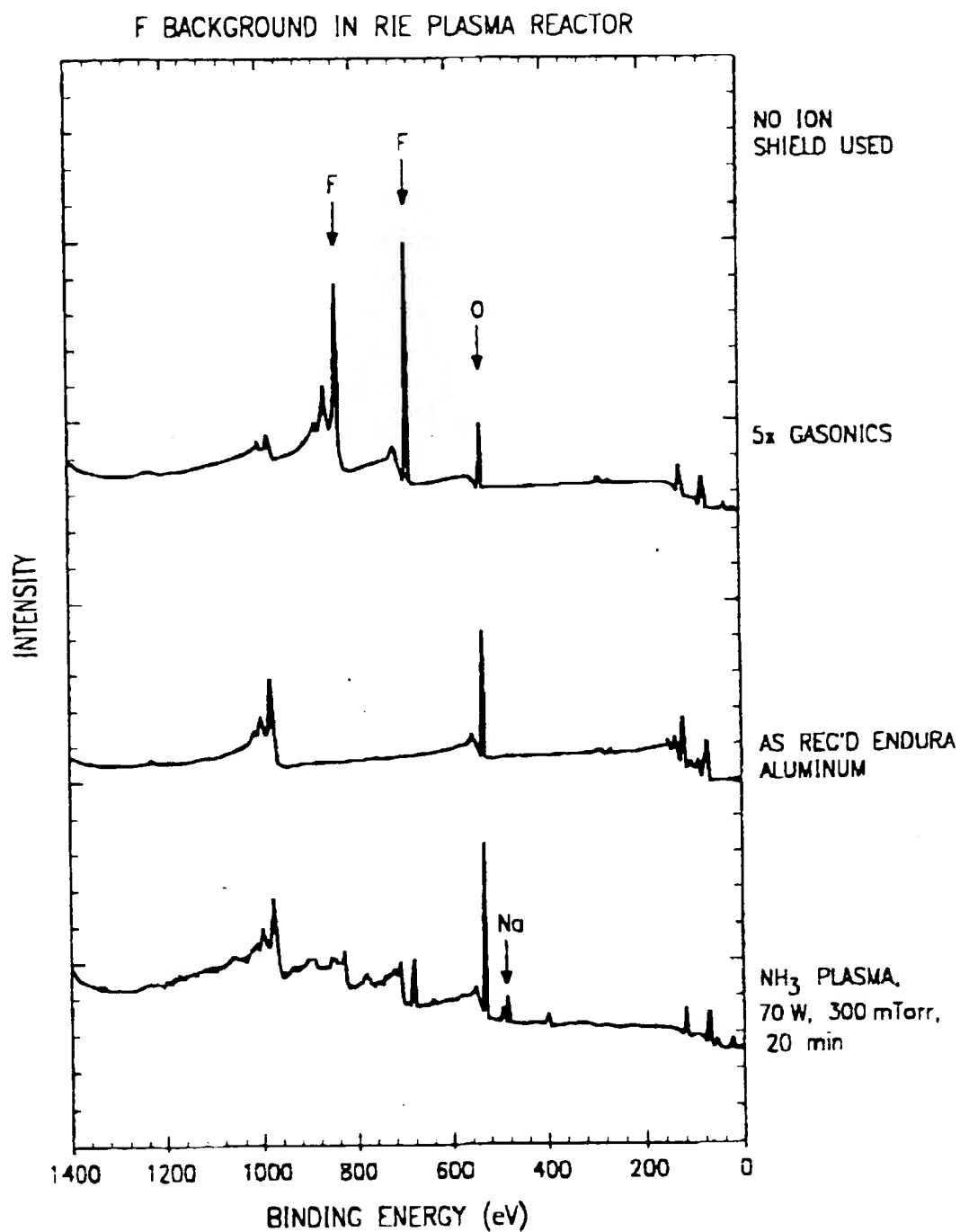


FIG. 6B

EFFECTS OF IONS IN PLASMA REACTOR

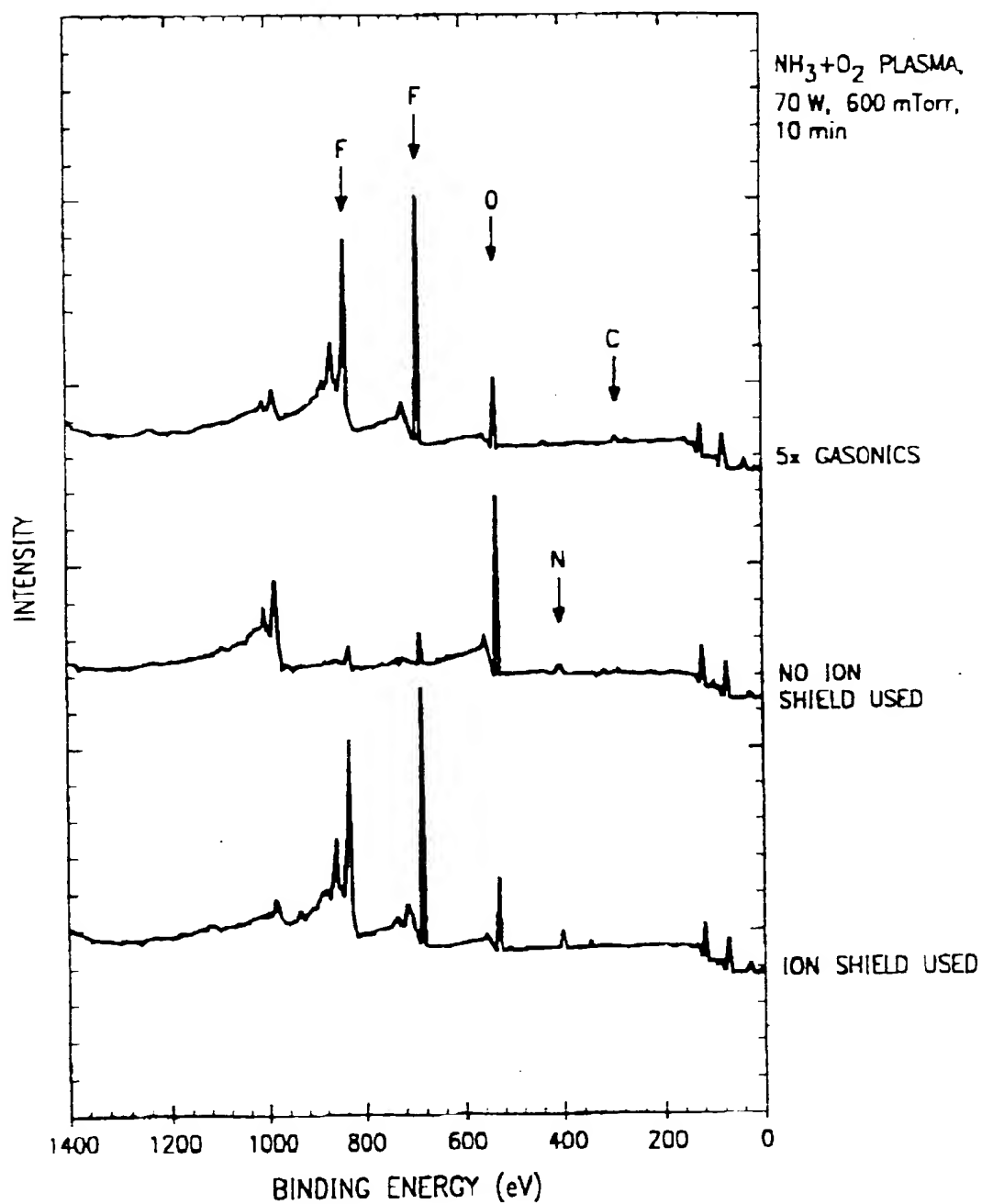


FIG. 6C

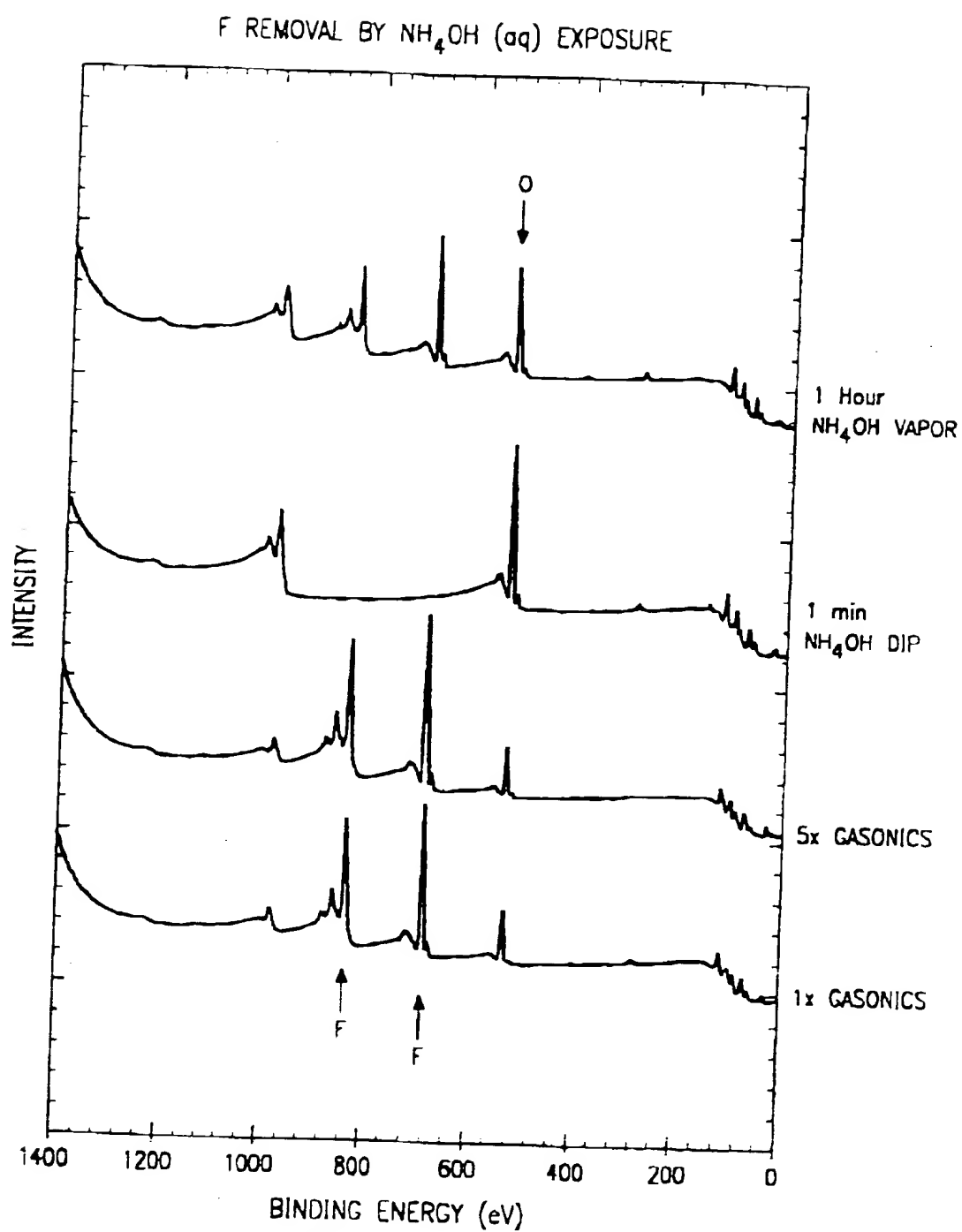
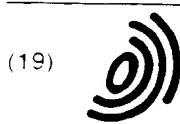


FIG. 6D





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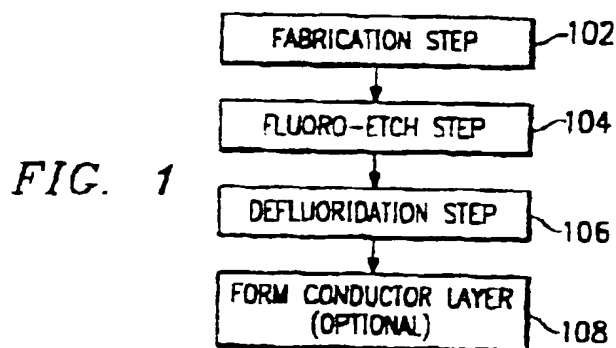
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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 97 31 0064

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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The present search report has been drawn up for all claims			

EP FORM 1503 (01-1994) (C1)

Place of search THE HAGUE	Date of completion of the search 22 October 1998	Examiner Nicke, K
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure F: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons S: member of the same patent family, corresponding document		